Contents

Preface xvii
List of Contributors xxi

Part 1: Polysaccharides

1. Hyaluronic Acid: A Natural Biopolymer 3
   J. Schiller, N. Volpi, E. Hrabárová and L. Šoltés
   1.1 Glycosaminoglycans 4
   1.2 Hyaluronic Acid/Hyaluronan – Structure, Occurrence 7
   1.3 Hyaluronan Synthases 8
   1.4 Enzymatic Catabolism of Hyaluronan 10
   1.5 Oxidative Degradation of Hyaluronan 11
      1.5.1 Reaction of HA with HO' Radicals 13
      1.5.2 Reaction of HA with HOCl 17
      1.5.3 Reaction of HA with Peroxynitrite 18
   1.6 Hyaluronan Degradation under Inflammatory Conditions 19
      1.6.1 Generation of ROS under In Vivo Conditions 20
      1.6.2 Discussion of ROS Effects under In Vivo Conditions 21
      1.6.3 Cell-derived Oxidants and Their Effects on HA 22
      1.6.4 Synovial Fluids 23
      1.6.5 Extracellular Matrix 23
   1.7 Interaction of Hyaluronan with Proteins 24
      and Inflammatory Mediators
      1.7.1 HA Binding Proteins and Receptors 25
      1.7.2 HA Receptors – Cellular Hyaladherins 25
      1.7.3 Extracellular Hyaladherins 26
   1.8 Hyaluronan and Its Derivatives in Use 26
      1.8.1 Viscosurgery 27
      1.8.2 Viscoprotection 27
      1.8.3 Viscosupplementation 28
      1.8.4 Vehicle for the Localized Delivery of Drugs 28
          to the Skin
      1.8.5 Electrospinning for Regenerative Medicine 28
   1.9 Concluding Remarks 29
      Acknowledgements 29
      References 30
   B. S. Kaith, Hemant Mittal, Jaspreet Kaur Bhatia and Susheel Kalia
   2.1 Introduction 35
   2.2 Modification of Polysaccharides through Graft Copolymerization 36
      2.2.1 Graft Copolymerization Using Chemical Initiators 36
      2.2.2 Graft Copolymerization Using Radiations as Initiators 38
   2.3 Different Reaction Conditions for Graft Copolymerization 39
      2.3.1 In Air (IA) Graft Copolymerization 39
      2.3.2 Under Pressure (UP) Graft Copolymerization 39
      2.3.3 Under Vacuum (UV) Graft Copolymerization 40
      2.3.4 Graft Copolymerization Under the Influence of γ-Radiations 40
      2.3.5 Graft Copolymerization Under the Influence of Microwave Radiations (MW) 40
   2.4 Characterization of Graft Copolymers 42
      2.4.1 FT-IR 42
      2.4.2 ¹³C NMR 42
      2.4.3 SEM 44
      2.4.4 XRD 44
      2.4.5 Thermal Studies 45
   2.5 Properties of Polysaccharide Graft Copolymers 46
      2.5.1 Physical Properties 47
      2.5.2 Chemical Properties 48
   2.6 Applications of Modified Polysaccharides 49
      2.6.1 Sustained Drug Delivery 49
      2.6.2 Controlled Release of Fungicide 49
      2.6.3 Selective Removal of Water from Different Petroleum Fraction-water Emulsions 50
      2.6.4 Removal of Colloidal Particles from Water 50
      2.6.5 Graft Copolymers as Reinforcing Agents in Green Composites 50
   2.7 Biodegradation Studies 51
   2.8 Conclusion 53
   References 53

3. Natural Polysaccharides: From Membranes to Active Food Packaging 59
   Keith J. Fahnestock, Marjorie S. Auster and Caroline L. Schauer
   3.1 Introduction 59
   3.2 Polysaccharide Membranes 60
      3.2.1 Permselective Membranes 61
      3.2.2 Ionically Conductive Membranes 61
      3.2.3 Polysaccharide Polymers 63
4. Starch as Source of Polymeric Materials

Antonio José Felix Carvalho

4.1 Introduction 81
4.2 Starch Structure 83
4.3 Non-food Application of Starch 86
4.4 Utilization of Starch in Plastics 87
4.5 Some Features of the Physical Chemistry of Thermoplastic Starch Processing 89
4.6 Recent Developments in Thermoplastic Starch 92
4.7 Reactive Extrusion 93
4.8 Conclusion 94
Acknowledgement 95
References 95

5. Grafted Polysaccharides: Smart Materials of the Future, Their Synthesis and Applications

Gautam Sen, Ashoke Sharon and Sagar Pal

5.1 Introduction: Polysaccharides as a Material of the Future 99
5.2 Modified Polysaccharides 100
5.2.1 Modification by Insertion of Functional Groups onto the Polysaccharide Backbone 100
5.2.2 Modification by Grafting of Chains of Another Polymeric Material onto Polysaccharide Backbone 101
5.3 Characterization of Grafted Polysaccharides 110
5.3.1 Intrinsic Viscosity 110
5.3.2 Elemental Analysis 111
5.3.3 FTIR Spectroscopy 112
5.3.4 Scanning Electron Microscopy (SEM) Analysis 114
5.3.5 Thermo Gravimetric Analysis (TGA) 115
5.4 Application of Grafted Polysaccharides
   5.4.1 Application as Viscosifier
   5.4.2 Application as Flocculant for Water Treatment
   5.4.3 Application as Matrix for Controlled Drug Release
5.5 Conclusion
References

6. Chitosan: The Most Valuable Derivative of Chitin
   Debasis Sahoo and P.L. Nayak
   6.1 Introduction
   6.2 Polysacharide
   6.3 Sources of Chitin and Chitosan
   6.4 Composition of Chitin, Chitosan and Cellulose
   6.5 Chemical Modification of Chitin and Chitosan
   6.6 Chitin – Chemical Modification
   6.7 Chitosan – Chemical Modification
      6.7.1 O-/N-carboxyalkylation
      6.7.2 Sulfonation
      6.7.3 Acylation
      6.7.4 Sugar-Modified Chitosan
   6.8 Depolymerization of Chitin and Chitosan
      6.8.1 Chemical Methods
      6.8.2 Physical Methods
      6.8.3 Enzymatic Methods
      6.8.4 Graft Copolymerization
      6.8.5 Chitosan Crosslinking
   6.9 Applications of Chitin and Chitosan
   6.10 Bio-medical Applications of Chitosan
      6.10.1 Gene Therapy
      6.10.2 Enzyme Immobilization
      6.10.3 Antioxidant Property
      6.10.4 Hypocholesterolemic Activity
      6.10.5 Wound-healing Accelerators
      6.10.6 Artificial Kidney Membrane
      6.10.7 Drug Delivery Systems
      6.10.8 Blood Anticoagulants
      6.10.9 Artificial Skin
   6.11 Miscellaneous Applications
   6.12 Antimicrobial Properties
   6.13 Film-forming Ability of Chitosan
   6.14 Function of Plasticizers in Film Formation
   6.15 Membranes
   6.16 In Wastewater Treatment
   6.17 Multifaceted Derivatization Potential of
      Chitin and Chitosan
   6.18 Conclusion
References
Part 2: Bioplastics and Biocomposites

7. Biopolymers Based on Carboxylic Acids Derived from Renewable Resources
*Sushil Kumar, Nikhil Prakash and Dipaloy Datta*

7.1 Introduction 169
7.2 Carboxylic Acids: Lactic- and Glycolic Acid
  7.2.1 Lactic- and Glycolic Acid Production 170
7.3 Polymerization of Lactic- and Glycolic Acids
  7.3.1 Polymerization of Lactic Acid 173
  7.3.2 Polymerization of Glycolic Acid 178
7.4 Applications 180
7.5 Conclusions 181
References 181

8. Characteristics and Applications of Poly (lactide)
*Sandra Domenek, Cécile Courgneau and Violette Ducruet*

8.1 Introduction 183
8.2 Production of PLA
  8.2.1 Production of Lactic Acid 184
  8.2.2 Synthesis of PLA 186
8.3 Physical PLA Properties 190
8.4 Microstructure and Thermal Properties
  8.4.1 Amorphous Phase of PLA 192
  8.4.2 Crystalline Structure of PLA 193
  8.4.3 Crystallization Kinetics of PLA 194
  8.4.4 Melting of PLA 197
8.5 Mechanical Properties of PLA 197
8.6 Barrier Properties of PLA
  8.6.1 Gas Barrier Properties of PLA 199
  8.6.2 Water Vapour Permeability of PLA 201
  8.6.3 Permeability of Organic Vapours through PLA 202
8.7 Degradation Behaviour of PLA
  8.7.1 Thermal Degradation 203
  8.7.2 Hydrolysis 204
  8.7.3 Biodegradation 206
8.8 Processing 208
8.9 Applications
  8.9.1 Biomedical Applications of PLA 210
  8.9.2 Packaging Applications Commodity of PLA 211
  8.9.3 Textile Applications of PLA 214
  8.9.4 Automotive Applications of PLA 215
  8.9.5 Building Applications 215
  8.9.6 Other Applications of PLA 216
8.10 Conclusion 217
References 217
9. Biobased Composites and Applications
    Smita Mohanty and Sanjay K. Nayak
    9.1 Introduction 225
    9.2 Biofibers: Opportunities and Limitations 226
        9.2.1 Chemical Composition of Biofibers 228
        9.2.2 Surface Modification and Characterization of Biofibers 232
        9.2.3 Physical and Mechanical Properties of Biofibers 234
    9.3 Biobased Composites: An Overview 235
        9.3.1 Biobased Composites of Sisal Fiber Reinforced Polypropylene 237
        9.3.2 Innovations in Biobased Hybrid Composites 246
        9.3.3 Prototype Development and Future Recommendations 262
    9.4 Conclusion and Future Prospects 262
    References 263

Part 3: Miscellaneous Biopolymers

    Vandana Singh and Pramendra Kumar
    10.1 Introduction 269
    10.2 Cassia Seed Gums Based Flocculants 271
        10.2.1 Cassia angustifolia 272
        10.2.2 Cassia javanica 273
        10.2.3 Cassia tora 276
        10.2.4 Mechanism of Dye Removal by Flocculants 276
    10.3 Cassia Seed Gums Based Metal Sorbents 277
        10.3.1 Cassia grandis 278
        10.3.2 Cassia marginata 280
        10.3.3 Cassia javanica 283
    10.4 Other Grafted Cassia Seed Gums 285
        10.4.1 Cassia pudibunda 286
        10.4.2 Cassia occidentalis 286
        10.4.3 Cassia siamea 286
    10.5 Conclusion 286
    References 287

11. Bacterial Polymers: Resources, Synthesis and Applications
    GVN Rathna and Sutapa Ghosh
    11.1 Introduction 291
    11.2 Diverse Bacterial Species 295
        11.2.1 Polysaccharides 295
        11.2.2 Proteins 299
        11.2.3 Protein-polysaccharide and Lipopolysaccharides 299
        11.2.4 Polyesters 300
11.3 Methods to Obtain Bacterial Polymers 302
  11.3.1 Conventional Methods (extraction/isolation) 302
  11.3.2 Biosynthesis Methods 305

11.4 Tailor-made Methods 307

11.5 Applications 309
  11.5.1 Biomedical Applications 309
  11.5.2 Industrial Application 311
  11.5.3 Food Applications 311
  11.5.4 Agricultural Application 312

11.6 Conclusion and Future Prospective of Bacterial Polymers 312

References 312

12. Gum Arabica: A Natural Biopolymer 317
  A. Sarkar

12.1 Introduction 317
  12.1.1 Natural Gums, Sources and Collection 319

12.2 Chemistry of Gum Arabica 320
  12.2.1 Potential Use as Material 321

12.3 Electroactivity of Gum 321
  12.3.1 Ionic Conduction in Electroactive Material 322
  12.3.2 Conduction Mechanism 323
  12.3.3 Ion Transference Number 323
  12.3.4 Conducting Ion Species in Gum Arabica 324
  12.3.5 Carrier Mobility in Gum Arabica 324

12.4 Method of Characterization 325
  12.4.1 Microscopic Observation 325
  12.4.2 Microscopic Observations 326
  12.4.3 Thermodynamic Analysis 328
  12.4.4 Electrical Polarization and A.C. Conductivity 330

12.5 Electronic or Vibrational Properties 338

12.6 Enhancement of Electroactivity 342

12.7 Application Potential in Material Science 344
  12.7.1 Gum Arabica and Its Scope of Application 344
  12.7.2 Biopolymer Gel 345
  12.7.3 Nanocomposites 351
  12.7.4 Metallic Sulphide Nanocomplex of Gum Arabica 352
  12.7.5 Development of Carbon Nanoparticle 356
  12.7.6 Photosensitive Complex 359

12.8 Development of Biopolymeric Solar Cells 364

12.9 Biomedical-like Application 370

12.10 Conclusion 374
  Acknowledgements 374
  References 374

13. Gluten: A Natural Biopolymer 377
  S. Georgiev and Tereza Dekova

13.1 Introduction 378
13.2 Gliadins
   13.2.1 Genetics and Polymorphism 384
13.3 Glutenins
   13.3.1 Gluten Polymer Structure 388
   13.3.2 Polymeric Proteins 389
   13.3.3 Structure 391
   13.3.4 Relationship to Wheat Quality 392
13.4 LMW-GS
   13.4.1 Structure 393
   13.4.2 Molecular Characterization of LMW-GS Genes 395
13.5 MALDI/MS: A New Technique Used to Analyze
   the Proteins in Plants 397
13.6 Albumins and Globulins 397
13.7 Wheat Gluten and Dietary Intolerance 398
13.8 Conclusion 399
References 399

14. Natural Rubber: Production, Properties and Applications 403
   Thomas Kurian and N. M. Mathew
14.1 Introduction 403
14.2 Rubber Yielding Plants 404
14.3 History 404
14.4 Plantation Rubber 406
14.5 Rubber Cultivation 407
   14.5.1 The Para Rubber Tree 407
   14.5.2 Agro-climatic Requirements 408
   14.5.3 Planting 408
   14.5.4 Disease Control 408
   14.5.5 Tapping and Collection of Crop 410
14.6 Biosynthesis of Rubber 412
14.7 Chemistry of Latex 413
14.8 Primary Processing 413
   14.8.1 Preserved and Concentrated Latex 414
   14.8.2 Ribbed Smoked Sheet 415
   14.8.3 Pale Latex Crepe and Sole Crepe 418
   14.8.4 Field Coagulum Crepe 418
   14.8.5 Technically Specified Rubber 419
14.9 Current Global Status of Production
   and Consumption 421
14.10 Properties of NR 421
14.11 Blends of Natural Rubber 423
   14.11.1 Blends of Natural Rubber with Thermoplastics 423
   14.11.2 Preparation of Thermoplastic Natural Rubber 423
   14.11.3 Properties and Applications of TPNR 423
14.12 Modified Forms of Natural Rubber 424
   14.12.1 Introduction 424
   14.12.2 Hydrogenated Natural Rubber 424
14.12.3 Chlorinated Natural Rubber 424
14.12.4 Cyclized Natural Rubber 425
14.12.5 Graft Copolymers Based on Natural Rubber 425
14.12.6 Epoxidized Natural Rubber 426
14.12.7 Ionic Thermoplastic Elastomers Based on Natural Rubber 427

14.13 Introduction to the Manufacture of Rubber Products 428
14.13.1 Processing Methods 429
14.13.2 Vulcanization Techniques 431

14.14 Applications of Natural Rubber 431
14.14.1 Dry Rubber Products 431
14.14.2 Latex products 432

14.15 Natural Rubber, a Green Commodity 432
14.16 Conclusions 433
References 433

15. Electronic Structures and Conduction Properties of Biopolymers 437
Mohsineen Wazir, Vinita Arora and A.K. Bakhshi

15.1 Introduction 437
15.2 Electronic Conduction in Proteins 438
15.2.1 Introduction 438
15.2.2 Investigations of Electronic Structure and Conduction Properties of Periodic and Aperiodic Polypeptides 439
15.2.3 Factors Affecting the Conduction Properties of Proteins 444

15.3 Electronic Conduction in DNA 447
15.3.1 Introduction 447
15.3.2 Mechanisms of Electron Transfer in DNA 447
15.3.3 Factors Affecting the Conductivity of DNA 448
15.3.4 Investigation of the Electronic Structure of DNA Base Stacks 448

15.4 Conclusions 453
References 454

Part 4: Biopolymers for Specific Applications

16. Applications of Biopolymers in Agriculture with Special Reference to Role of Plant Derived Biopolymers in Crop Protection 461
S. Niranjan Raj, S.N. Lavanya, J. Sudisha, and H. Shekar Shetty

16.1 Introduction 461
16.2 Biopolymers 462
16.3 Sources of Biopolymers 463
16.3.1 Plants 463
16.3.2 Microbes 464
16.3.3 Animals 466
16.3.4 Agricultural Wastes 466
16.3.5 Fossils 466
16.4 Application of biopolymers in agriculture 467
16.5 Seed coating for value addition 469
16.6 Plant Derived Biopolymers in Plant Growth Promotion 470
16.7 Plant Derived Biopolymers in Plant Disease Management 474
16.8 Integrated Use of Plant Gum Biopolymers 476
16.9 Transgenically Produced Biopolymers 477
16.10 Conclusions and Future Prospects 478
References 479

17. Modified Cellulose Fibres as a Biosorbent for the Organic Pollutants 483
   Sami Boufi and Sabrine Aïila
17.1 Introduction 483
17.2 Cellulose Structure 484
   17.2.1 Molecular Level 484
   17.2.2 Supramolecular Structure 485
   17.2.3 Ultrastructure 486
17.3 Application of Natural Lignocellulosic Materials as Adsorbents for Organic Pollutants 488
17.4 The Use of Modified Cellulose Fibres as a Sorbent for the Organic Pollutants Removal 491
   17.4.1 Adsorption of Model Organic Compounds on Surfactant Treated Cellulose Fibres 491
   17.4.2 Different Strategies of Surface Chemical Modification of Cellulose Fibres 497
17.5 Adsorption Properties of Modified Cellulose Fibres 509
   17.5.1 Adsorption of Herbicides 512
17.6 Adsorption Isotherm Modellisation 514
17.7 Thermodynamic Parameters 516
17.8 Adsorption Kinetic Modelling 516
17.9 Column Studies 519
17.10 Column Regeneration 519
17.11 Investigation of Adsorption Mechanisms by Laser Induced Luminescence 520
17.12 Conclusion 521
   References 522

18. Polymers and Biopolymers in Pharmaceutical Technology 525
   István Erős
18.1 Introduction 525
18.2 Purpose of the Use of Polymers in Pharmacy and Medicine 526
   18.2.1 Active Substances 527
18.2.2 Bases for Preparations 528
18.2.3 Filling, Binding, Stabilizing and Coating Materials 528
18.2.4 Polymers Controlling Drug Release 529

18.3 Administration of Active Substances through the Mucosa of Body CAVITIES WITH THE HELP OF POLYMERS AND BIOPOLYMERS 547
18.3.1 Mucoadhesion 548
18.3.2 Mucoadhesive Preparations in the Gastrointestinal Tract 549
18.3.3 Drug Administration through the Nasal Mucosa 550
18.3.4 Mucoadhesive Preparations on the Mucosa of the Eye 551
18.3.5 Mucoadhesive Preparations in the Rectum and in the Vagina 552

18.4 Conclusion 553
References 554

19. Biopolymers Employed in Drug Delivery 559
Betina Giehl Zanetti Ramos
19.1 Introduction 559
19.2 The Most Studied Biopolymers in Drug Delivery 560
19.2.1 Cellulose Derivatives 561
19.2.2 Biopolymers from Marine Source 563
19.2.3 Others Polysaccharides 565
19.2.4 Polyhydroxyalkanoates 569
19.2.5 Biopolymers from Proteins 570
19.3 Conclusion 571
References 571

20. Natural Polymeric Vectors in Gene Therapy 575
Patit P. Kundu and Kishor Sarkar
20.1 Introduction 575
20.2 Cationic Polymers 577
20.3 Natural Polymers as Nonviral Vectors in Gene Therapy 578
20.3.1 Chitosan 578
20.3.2 Gelatin 592
20.3.3 Alginate 593
20.3.4 Arginine 594
20.3.5 Collagen 596
20.4 Conclusions 599
References 599

Index 605